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*HCX₃ + Oxidizable organic
dye - bleached when
exposed + heated (fix)* No. 779,239



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INFORMATION RECORDING

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This invention pertains generally to the recording of an irreversible image by selectively bleaching a suitable colored recording member with activating photoradiation. More particularly, the invention pertains to an information recording system for irreversibly removing color from a solid recording member to produce a clear and detailed image therein solely by exposing the member to activating photoradiation.

Photographic bleaching has been formerly accomplished with certain dyes wherein an image pattern has been established either directly in response to activating photo-radiation or after exposure and suitable development with solvents, heat, or other external means. Many of these processes have not been commercially accepted because spectral sensitivity of the recording member is restricted to limited regions of the ultraviolet or infrared spectrum. The unacceptability of other bleaching systems has been attributed to a requirement for developing agents which are corrosive or toxic materials often requiring special handling procedures. Still other "bleach-out" systems have limited resolution capability which lowers the information storage density of the particular light-sensitive composition. It would represent substantial progress in the photographic arts to provide a "bleach-out" recording system which is substantially free from the above recited limitations.

It is one important object of the invention, therefore, to provide a recording member containing a



color dye which can be selectively bleached solely by exposure to a modulated beam of activating photoradiation.

5 It is still another important object of the invention to provide a simpler recording system than is now generally available for producing a permanent "bleach-out" image in a solid recording member.

10 Still another important object of the invention is to provide a simple recording member comprising a dispersion of a color dye with a particular light-sensitive material capable of permanent selective bleaching after exposure to activating photoradiation.

15 A still further important object of the invention is to provide a recording process whereby a bleached dye image is produced solely by exposing the recording member to selective photoradiation or by merely sensitizing the recording member with the selective photoradiation and thereafter heat-developing a permanent final image.

20 These and other important objects and advantages of the invention will be apparent from the following detailed description of the invention.

25 Briefly, the present recording compositions each comprise the combination of a polyhalogenated organic compound having each halogen atom bonded to a carbon atom which has no more than two hydrogen atoms bonded thereto with an oxidizable organic dye which can be bleached when exposed to activating photoradiation in the presence of the polyhalogenated organic compound. The recording compositions may comprise simple admixtures of the recited materials in the form of coatings on substrate layers or dispersions of these materials in an inert supporting matrix of

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optically transparent material. Selective bleaching of a recording composition may be accomplished with exposure to activating photoradiation with the pattern to be recorded for a sufficient period of time to produce bleaching.

5 Alternately, the bleached image may be provided by sensitizing the recording member with shorter time periods of exposure insufficient to produce color change and thereafter heating the sensitized medium to produce bleaching.

Many of the present recording compositions are
10 sensitive to radiation in the visible portion of the spectrum and permit recording with conventional systems now used in general purpose photographic applications. More particularly, ordinary optical projection systems may be used to copy an image from a transparent recording, such
15 as an exposed photographic negative, and the like, onto one of the present recording members. Since a "bleach-out" image may be produced by simple light exposure, there is no need to modify existing projection equipment in order to produce a visible image. Use of conventional photographic equipment for image copying in this manner provides
20 an extremely simple system of recording. A desired image may be reproduced with the present recording compositions on a wide variety of substrates including paper, textiles, plastic films, metal plates, ceramic surfaces, and other
25 substrate media. To copy an image on a particular substrate in the general manner outlined, the substrate first may be coated with a coating composition of the recording material and the coating thereafter may be exposed to activating photoradiation in the pattern to be copied.
30 While the image produced by light exposure is reasonably

stable to normal ambient lighting for useful periods, continued exposure of the recording medium to daylight conditions will eventually produce image defects such as contrast loss, and the like. The image may be "fixed" to avoid this problem by heating the image-bearing recording member sufficiently to volatilize the remaining poly-halogenated organic compound in the recording compositions.

Particularly, useful recording members may be prepared simply by dispersing the present recording compositions in a normally solid organic polymer film. The final recording film may be prepared from an organic liquid solvent solution of the recording composition and a compatible optically transparent synthetic organic polymer whereby a liquid film is cast from the solution and the solvent removed therefrom by conventional procedure. Unsupported flexible films of this recording material may be used directly in cinematographic applications or the films may be adhered to flexible transparent backing layers for greater mechanical support. Since many of the present recording compositions may be adequately sensitized for image production by irradiation lasting only a few seconds, or less with subsequent heat-development producing the final bleached image, it is within contemplation of the invention to employ the present compositions as true negative photographic materials for use in camera-type devices. Heat development of a sensitized composition after photoradiation in the camera device is further conducive to construction of a recording apparatus which may also be employed to project the final recorded image onto a viewing surface.

Having described the invention generally, it can be practiced in its preferred embodiments as illustrated in the following examples and subsequent discussion thereon. Where parts and percentages appear hereinafter in the specification, they refer to parts and percentages by weight unless otherwise specified.

Example 1

A suitable recording film may be obtained from a liquid film-forming polymer solution containing the recording composition by casting a continuous film and removing the liquid from the cast film. The liquid coating composition may be prepared by mixing 2 parts iodoform, 0.2 part indophenol blue, and 10 parts polystyrene resin in 100 parts benzene at room temperature with agitation until a uniform solution is obtained. A useful polystyrene material for the recording composition possesses an average molecular weight of approximately 20,000 and a softening temperature of approximately 85°C. The blue-colored recording film is obtained conveniently from the liquid coating composition by casting an approximately 0.002 inch thick film of the composition on a glass plate and drying the film. The solid coating may be exposed to activating photoradiation in situ or removed from the glass substrate for separate exposure.

Selective bleaching of the blue film in an image pattern may be produced directly by exposure of the film to activating photoradiation through a light transparent medium containing the image to be recorded. Accordingly, the film may be exposed to a 300-watt tungsten filament

lamp for approximately 60 seconds through an image-bearing photographic negative to produce a copy of the negative image on the recording film. Those portions of the recording film receiving illumination through the negative are selectively bleached from a uniform deep blue color of the original film to various shades of lighter blue. Some portions of the film experience loss of all color depending upon the amount of illumination received from the negative. A full shade tone image is formed on the recording film corresponding in a point-by-point relationship with the image of the photographic negative. Visual comparison for the degree of shade tones (or gray scale) in a representative recorded image with an Eastman Kodak Photographic Steptable Model 1A Comparater having an optical density range 0.05-3.5 revealed eleven shades of gray in the compared image compared to twelve shades of gray for the standard. Use of a "compatible" polymer for the recording film wherein both materials of the recording composition are soluble produces a recording medium having resolution capability on a molecular scale so that the recording contains all the detail of the projected optical image. Consequently, use of the term "compatible" hereinafter in the specification and claims is intended to describe a polymer material advantageously employed as a dispersing medium for the recording composition which is a solvent for each of the recording materials.

Permanent fixing of the image produced in the above described manner may be obtained by heating the exposed recording member to 120°C for approximately 10 minutes. Sufficient heating of a recording member still containing

the light-sensitive polyhalogenated organic compound is necessary to remove remaining amounts of this material which could produce further color loss in the recording member upon additional irradiation. The degree of heating necessary for fixing an image is understandably dependent upon the volatility characteristics of the particular polyhalogenated organic compound in the recording medium and suitable time-temperature conditions for the operation may be established in conventional fashion.

Example 2

10 A recording film may be prepared consisting of 15 parts of erythrosine, 12 parts iodoform, and 100 parts of a commercially available polymethyl methacrylate material. Exposure of the solid film to a selective pattern of ultraviolet radiation for approximately 2 minutes produces a
15 bleached image in the recording film exhibiting substantially the same optical characteristics as the recorded image of the preceding example.

Example 3

20 A recording film may be prepared having the same general composition as the recording member of Example 1 except that for the polystyrene dispersing medium there was substituted an equal amount of polyvinylidene chloride polymer having a softening temperature in the range 65-70°C and a room temperature viscosity of approximately 70 centipoises in a 20 percent solids acetone solution.
25 Exposure of the solid recording member to radiation emitted from a 300-watt tungsten filament lamp for approximately

30 seconds produces a bleached image exhibiting substantially the same optical characteristics as the recorded image in Example 1.

Example 4

As previously mentioned hereinbefore in the specification, a bleached image may be produced by an alternate procedure wherein the recording member is sensitized with photoradiation in the image pattern to produce a latent image which is bleached with heat to provide a reproduction of the projected radiation. Suitable sensitization of the recording member is provided by exposure to activating photoradiation for insufficient time periods to result in any substantial color loss in the recording medium. Accordingly, a recording film having the composition of Example 1 may be exposed to an image pattern of the photoradiation emitted from a 300-watt projector for approximately 30 seconds which is an adequate exposure period to sensitize the recording member but not produce a distinct image in those portions of the recorded film receiving illumination. A latent image having all the significant details of the projected illumination is produced in the recording member by the irradiation. Subsequent heating of the exposed recording member to a temperature of approximately 120°C for a time period of around 10 minutes produces a permanent bleached image in the film. Recording of an image in the manner described is adapted for general purpose photographic applications because of the relatively short exposure periods necessary for image production. The above results also point out that simultaneous

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development and fixing of the final image may be obtained in a single heating step.

Example 5

To illustrate the utility of organic dyestuffs generally in the practice of the invention with the exception of pigment dyes or intensification dyes, a recording member may be prepared employing a representative member from the merocyanine class of organic dye materials. Accordingly, 0.2 part of 3-ethyl-5-[(3,3'-dimethyl-1-phenyl-2(3H)indolylidene)-2-butenylidene]-rhodamine, 20 parts iodoform, and 100 parts of the aforementioned polystyrene material may be dissolved in benzene and solid films cast from the liquid coating composition, all as previously described, to provide the final recording member. Exposure of the film to conventional flashbulb radiation produces bleaching in those areas receiving the photoradiation.

Example 6

Still different composition dyes may be employed successfully for preparation of satisfactory recording films in the same general manner as hereinbefore described. Thus, representative members of still other chemical dye classes may be dissolved in a film-forming polymeric medium along with the polyhalogenated organic compound to form a recording composition. Suitable recording films may be prepared in this manner containing 2 parts of the particular dye substance, 10 parts iodoform, and 100 parts of the same polyvinylidene chloride polymer described in Example 3. Results obtained by selectively exposing the

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individual recording members to ultraviolet radiation are listed in the table below:

Table

	<u>Organic Dye</u>	<u>Exposure Time</u>	<u>Results</u>
5	Brilliant Green	2 minutes	Bleached film
	Methyl Orange	2 minutes	Bleached film
	Quinalizarine	10 minutes	Bleached film
	Indigo	10 minutes	Bleached film

10 The above successful results indicate that all major classes of organic dye materials may be selectively bleached in accordance with the principles of the invention. Furthermore, the chemical composition of the organic polymer material selected for film preparation is not deemed critical for production of a bleached image since the
15 polymer's principal function in the recording composition is to disperse the recording materials. For this reason, satisfactory polymers may be selected from the broad class of inert organic resin film-formers which are optically transparent to the particular photoradiation employed in
20 recording. Since greater image resolution is obtained with molecular dispersion of the recording materials, the preferred polymers also dissolve both recording materials.

Useful polyhalogenated organic compounds for preparation of the present recording compositions may be
25 selected from the broad class of photosensitive carbon-to-carbon bonded compounds containing at least two halogen atoms which produce photolytic halogen in the dispersing medium when exposed to activating photoradiation. The chemical composition of these materials may be further defined as

organic compounds containing a plurality of halogen atoms bonded to one or more carbon atoms having no more than two hydrogen atoms bonded thereto. The preferred polyhalogenated organic compounds may be still further characterized structurally as having a plurality of halogen atoms bonded to the same carbon atom for greater reactivity in the desired liberation of photolytic halogen upon photoradiation. Photolytic halogen-producing organic compounds are known and include such diverse chemical compositions as polyhalogen-substituted alkyl hydrocarbons, for example, iodoform, methylene iodide, and tetraiodoethylene; mononuclear polyhalogenated aromatic compounds such as chloranil; and alicyclic polyhalogenated organic compounds such as tetraiodocyclohexane. Especially preferred polyhalogenated organic compounds are halogen-substituted alkyl hydrocarbons which are readily soluble in organic solvents and polymeric suspending media used for the recording member to permit molecular dispersion of the material for greater resolution capability in recording. The preferred materials are also generally sensitive to photoradiation in the visible spectrum so as to permit photocopying and the like, using ordinary sources of illumination. The preferred polyhalogenated alkyl hydrocarbons exhibit faster response to illumination generally and for a given period of exposure, also generally yield a bleached image having more gray scale than other polyhalogenated organic compounds mentioned. Iodoform is an especially preferred material which exhibits all of the aforementioned desirable characteristics as well as being less volatile than many other polyhalogenated organic compounds. The latter characteristic

minimizes loss of the light-sensitive agent during storage of the recording member before use.

Useful organic dyes for the present recording compositions can be characterized generally as colored materials which when dispersed in a dye receptive medium, together with a polyhalogenated organic compound, impart general coloration to the entire medium subject to selective color change upon photoradiation. The dye material itself may be further characterized consistent with the preceding description as a colored organic compound which undergoes irreversible color change generally to a colorless product through reaction with photolytic halogen generated in the recording medium. Still another important characteristic of the present dye systems for recording is distinctive localization of color change as compared with other "bleach-out" systems wherein the photochemical reaction, after generation, is prone to continue to a much greater degree. The effect of this distinction is reflected in resolution capability of a particular dye system with better resolution being achieved by greater localization of the photochemical reaction.

While the exact mechanism of the present photochemical conversion is not known with precision at the present time, the nature of the reaction is deemed to involve removal or modification of the chromophore and/or oxychrome groups in the dye material by photolytic halogen to produce an irreversible oxidation product. This is not to imply that fully exposed portions of the recording member are rendered absolutely colorless since the final coloration observed after exposure is that of the environment. It

should further be pointed out that while most of the useful dyes are rendered substantially colorless after exposure to sufficient photoradiation, some dyes may be oxidized selectively to products having different colors than the original materials. Either type color change is acceptable for recording, however, since the photo-oxidation produces a distinct contrast image in the recording medium.

Useful organic dyes having the aforementioned desirable characteristics can be selected from the broad class of chromogens which are colored by molecular absorption of light including triphenylmethane dyes such as brilliant green and eriochlorine; azo dyes such as methyl red and methyl orange; anthraquinone dyes such as quinizarin and alizarin red S; thiazine dyes such as methylene blue; quinoline dyes such as pyranol; xanthene dyes such as rose bengal and erythrosine; merocyanine dyes; indophenol dyes; and indigo. The indophenol and merocyanine dyes are preferred as having a faster response to the activating photoradiation than the other classes of dye compositions mentioned together with a broader spectral response region which includes the visible spectrum. On the other hand, the spectral sensitivity of bleachable dyes generally may be increased without loss of desirable characteristics in the recording composition by incorporation therein of effective amounts of such known photosensitizers as diphenylamine, dimethylaniline, and other organic base materials.

While the particular proportions of the active materials in the present recording compositions have not been found especially critical for preparation of a satisfactory image in accordance with the previously

described procedures, from a practical standpoint it will be desirable to limit the concentration of active materials to only that necessary for image production. Generally, in a polymeric suspending medium there is imparted sufficient coloration to permit visible recognition of a bleached image at dye concentrations as low as 0.1 parts organic dye per 100 parts of the particular polymer employed. Bleaching of the dye in a recording composition is most readily accomplished at excess molar ratios of the polyhalogenated organic compound to the dye in the composition, although it will be advisable to maintain the concentration of the polyhalogenated organic compound in the preferred recording members at the minimum effective level necessary to effect distinct color contrast because of other considerations. More particularly, a soluble polyhalogenated organic compound often serves as a plasticizer for the polymeric dispersing medium in the preferred recording members so that it is desirable to limit the ratio of polyhalogenated organic compound in the composition to below about 25 parts per 100 parts of polymer. At greater concentrations of polyhalogenated organic compound in these recording compositions, the final solid film remains tacky at ordinary ambient conditions which requires special handling procedures to avoid possible damage of the recording member.

From the foregoing description, it will be apparent that a general system of recording information as a "bleach-out" image has been provided. It is not intended to limit the invention to the preferred embodiments above shown, however, since it will be obvious to those skilled in the art that certain modifications of the present teachings

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can be made without departing from the true spirit and
scope of the invention. For example, while the specific
activating photoradiation employed in the above embodiments
to recording images has been ultraviolet or visible
5 radiation for convenience and economy of operation, it is
also recognized that many of the suitable polyhalogenated
organic compounds are also sensitive to infrared light,
x-rays, gamma rays, and other penetrating radiation which
may be used to record in accordance with the aforementioned
10 principles. Likewise, it is within the contemplation of
the invention to employ multiple dye layers to achieve
full color recording by adaptation of known color photo-
graphy processes. It is intended to limit the present
invention, therefore, only to the scope of the following
15 claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An information-recording process which comprises:
exposing a recording member to activating photoradiation in the image pattern to be recorded for a sufficient time to sensitize the recording member, but to produce no substantial color change; and heating the exposed recording member sufficiently to produce selective bleaching in those areas of the recording member receiving the photoradiation, the recording member comprising a transparent solid film obtained from a compatible mixture of an optically clear synthetic organic film-forming polymer, a polyhalogenated organic compound having each halogen atom bonded to a carbon atom which has no more than two hydrogen atoms bonded thereto, and an oxidizable organic dye which can be bleached when exposed to the sensitizing photoradiation and subsequently heated.
2. An information-recording process which comprises:
exposing a recording member to activating photoradiation in the image pattern to be recorded for a sufficient time to sensitize the recording member, but produce no substantial color change; and heating the exposed recording member sufficiently to produce both selective bleaching in those areas of the recording member receiving the photoradiation and insensitivity of the recording member to any further photoradiation, the recording member comprising a transparent solid film obtained from a compatible mixture of an optically clear synthetic organic film-forming polymer, a polyhalogenated organic compound having each halogen atom bonded to a carbon atom which has no more than two hydrogen atoms bonded thereto, and an oxidizable organic dye which can be bleached when exposed to the sensitizing photoradiation and subsequently heated.